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Description

This invention relates to electrically conductive polymers. It further relates to a method for preparing an electrically conductive poly(arylene sulfide) film.

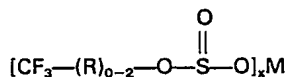
Commercial uses for electrically-conductive polymers and polymer compounds are increasing. Compositions having moderate conductivity (10^{-12} to 10^{-8} ohm $^{-1}$ cm $^{-1}$) are used where electrostatic discharge is important, such as in the computer and electronics industry. Semiconductive polymers (10^{-7} to 10^0 ohm $^{-1}$ cm $^{-1}$) are being developed for use in p-n junction devices, such as solar cells.

It is known that some thermoplastic polymers can be made electrically conductive by doping with a chemical agent. For example, electrical conductivity can be imparted to poly(phenylene sulfide) by doping the polymer with arsenic pentafluoride. Toxicity and stability would be considerations in the development of such a material, but the experiment suggests the potential for making this commercially-important material electrically conductive.

It is therefore an object of the invention to provide an electrically-conductive polymer. It is a further object to provide an article of manufacture containing an electrically conductive polymer. In a specific embodiment, it is an object of the invention to provide semiconductive or conductive poly(arylene sulfide).

Brief description of the invention

According to the invention, conductivity of a polymeric material is increased by the addition of a compound represented by the formula:

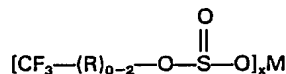


In one embodiment, a poly(arylene sulfide) is made more electrically conductive by the addition of zinc trifluoromethanesulfonate.

Detailed description of the invention

Any polymeric material which is capable of electrical conductivity with the addition of a doping agent is suitable for the invention composition and method. Such polymeric materials include thermoplastics such as polyethylene, polypropylene and copolymers incorporating these. Other, highly suitable polymers include poly(arylene sulfide)s and polysulfones. In general, such polymers include aromatic moieties having sulfide ($-\text{S}-$), ketone (CO) and/or sulfone (SO_2) linkages. Examples of such polymers include poly(phenylene sulfide), which can be prepared by the methods of U.S. 3,354,129 and 3,919,177, poly(arylene sulfide/sulfone), which can be produced by reacting sodium sulfide and bis (p-chlorophenyl) sulfone, and poly(benzophenone sulfide) prepared by reacting dichlorobenzophenone and sodium sulfide as described in Chemical Abstracts, Vol. 97, 216826Z.

The salt which is added to the polymeric material for imparting electrical conductivity can be represented by the formula



wherein M is a metal selected from Groups IB, IIB and VIII of the Periodic Table, x is the valence of M, and each R, if present, is selected independently from CH_2 and CF_2 . Examples of M include zinc, cadmium, mercury, copper, nickel and silver. The presently preferred material, for availability and effectiveness, is zinc trifluoromethanesulfonate, in which M is zinc and there are no R groups present.

Any method of incorporating the salt into the polymeric material is suitable as long as good dispersion is obtained. It is suitable, for example, to intimately mix by dry grinding the polymer in solid form with the salt in pure, solid form. The resulting mixture can then be molded by extrusion or compression means into electrically conductive objects, often in the form of film or thin sheet.

Poly(phenylene sulfide) film produced from compression molding is tan and opaque. Thermal analysis data suggest that the film is not crystallized to any significant extent. Representative thermal properties of a test sample included $T_g=87^\circ\text{C}$, $T_c=126^\circ\text{C}$, and $T_m=275^\circ\text{C}$.

The salt is incorporated into the polymer in an amount effective for increasing the electrical conductivity of the polymer. The amount will vary depending upon the particular polymer and salt used and the electrical conductivity desired. Levels of the salt of at least about 3 weight percent, preferably at least about 6 weight percent, are suitable. In general, the salt will make up from about 3 weight percent to about 12 weight percent, preferably about 6 weight percent to about 10 weight percent of the polymer and salt mixture.

It has been found that the purity of the chemical agent affects the level of imparted conductivity. It is therefore desirable to obtain the salt from a source which provides consistently pure reagents.

A molded article obtained from the polymer-salt mixture can be used for a variety of commercial purposes.

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Example I

A typical procedure is described for preparing films and evaluating additives. A mixture of 97 parts by weight poly(phenylene sulfide), the sample of which was an uncured PPS from Phillips Petroleum Company having a melt flow 20—65g/10 min at 316°C at 5Kg load according to modified ASTM D-1238, and 3 parts by weight zinc trifluoromethanesulfonate (Alpha Products) were intimately mixed by grinding in a mortar and pestle. The resulting powdered mixture was then dried in a vacuum oven at 110°C overnight. The dried powder was evenly spread into a thin 10 cm×10 cm (4 inch×4 inch) picture frame mold and compression molded between two pieces of aluminum foil at 315°C for 6 to 10 minutes at 240 MPa (35,000 psi) ram force. The frame, foil and contents were removed hot and allowed to cool slowly to room temperature to give a transparent or opaque film 10 cm×10 cm×0.063 cm (4 inches×4 inches×0.063 centimeters). Film samples were tested for conductivity by placing a 1.25 cm (0.5 inch) wide strip of film lengthwise across two strip terminals 1.25 cm (0.5 inch) apart and connecting them to a 45-volt cell battery. The current across the film sample was determined with a Keithley Electrometer, Model 610C. The voltage was also determined. From the measurements obtained, conductivity was calculated using the formulas

$$\sigma_v = \frac{1}{\rho_s \cdot t}$$

where

σ_v =conductance in ohms⁻¹ cm⁻¹
 ρ_s =surface resistivity in ohms/square
 t =film thickness, cm.,

and

$$\rho_s = \frac{R \cdot W}{l}$$

where

$R = \frac{\text{measured voltage}}{\text{measured amperage}}$

W =film width in cm.

l =film length in cm.

Based on the described procedure, the effect of zinc trifluoromethanesulfonate on the conductance of PPS film was determined. These results are listed in Table I where it can be shown that good conductance is obtained when about 6 to 10 weight percent of the zinc salt is present. The results show that at 10 weight percent (10 parts zinc salt, 90 parts PPS) the zinc salt provides more PPS conductance than the corresponding silver salt (Run 3) or zinc powder (Run 2). Compositions having 10⁻⁷ to 10⁰ ohm⁻¹ cm⁻¹ conductivity were considered semiconductive and useful in areas such as solar cells. The data also show that purity of the zinc trifluoromethanesulfonate additive to be important because film conductivities varied with different shipments or lots (compare runs 5 to 7).

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TABLE I.
Effect of zinc trifluoromethanesulfonate on the conductivity of PPS^(a)

5	Additive	Conductivity, ohm ⁻¹ cm ⁻¹
1.	no additive	5.9×10^{-12}
2.	10 wt. % zinc powder ^(b,f)	1.1×10^{-12}
10	3. 10 wt. % silver trifluoromethanesulfonate ^(c)	1.2×10^{-10}
4.	3 wt. % zinc trifluoromethanesulfonate ^(c)	3.5×10^{-11}
5.	5. 6 wt. % " " "	1.8×10^{-7}
15	6. 6 wt. % " " " ^(d)	4.7×10^{-11}
7.	7. 8 wt. % " " " ^(e)	3.9×10^{-11}
20	8. 10 wt. % " " " "	2×10^{-7}

^a. Poly(phenylene sulfide), Phillips Petroleum Co.

^b. Zinc dust from Mallinckrodt Chemical Co.

^c. Available from Alpha Products.

^d. A mixture of zinc salt from two lots.

^e. Zinc salt from a second lot.

^f. Dry blended with PPS, extruded at 316°C, ground in Wiley mill and compression molded to film.

Claims

- 30 1. A poly(arylene sulfide) composition characterized by containing at least one compound of the formula



wherein M is selected from the metals of Groups IB, IIB and VIII of the Periodic Table, x is the valence of M, and R is independently selected from CH₂ and CF₂, said compound being present in a quantity of about 3 weight percent to about 12 weight percent based on the mixture of poly(arylene sulfide) and compound.

- 40 2. The composition of claim 1 characterized in that M is a metal of Group IIB.
 3. The composition of claim 2 characterized in that M is zinc.
 4. The composition of claim 3 characterized in that said compound is zinc trifluoromethane sulfonate.
 5. The composition of any of the preceding claims characterized in that said compound is present in an amount of 6—10 weight percent; based on the weight of the composition.
 45 6. The composition of any of the preceding claims characterized in that said poly(arylene sulfide) comprises poly(phenylene sulfide); in particular wherein the poly(arylene sulfide) comprises at least two aromatic moieties joined by sulfide linkages.
 7. A method for increasing the electrical conductivity of a polymeric material characterized by dispersing in said polymeric material at least one compound of the formula



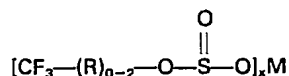
55 wherein M, x and R are as defined in claim 1.

8. The method of claim 7 characterized in that said compound and said polymer are as defined in any of claims 2 to 6.
 9. An article of manufacture produced from the composition of any of claims 1 to 6.
 10. The article of claim 9 in the form of a film characterized by having an electrical conductivity of at
 60 least about 10^{-7} ohm⁻¹ cm⁻¹.

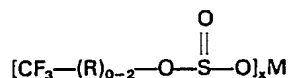
Patentansprüche

- 65 1. Poly(arylene-sulfid)-Zusammensetzung, dadurch gekennzeichnet, daß sie mindestens eine Verbindung der Formel

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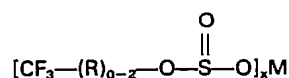
- 5 enthält, wobei M aus den Metallen der Gruppen IB, IIB, und VIII des periodischen Systems ausgewählt ist, x die Valenz von M darstellt, und R unabhängig aus CH₂ und CF₂ ausgewählt ist, wobei die Verbindung anwesend ist in einer Menge von etwa 3 Gew.% bis etwa 12 Gew.% bezogen auf das Gemisch von Poly(arylsulfid) und der Verbindung.
2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß M ein Metall der Gruppe IIB ist.
- 10 3. Zusammensetzung nach Anspruch 2, dadurch gekennzeichnet, daß M Zink ist.
4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Verbindung Zinktrifluoromethansulfonat ist.
5. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Verbindung in einer Menge von 6–10 Gew.%, bezogen auf das Gewicht der Zusammensetzung anwesend
- 15 ist.
6. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Poly(arylsulfid) Poly(phenylsulfid) enthält, insbesondere wobei das Poly(arylsulfid) mindestens zwei mit Sulfidbindungen verknüpfte aromatische Reste enthält.
7. Verfahren zum Erhöhen der elektrischen Leitfähigkeit eines polymeren Stoffes, dadurch
- 20 gekennzeichnet, daß man in dem polymeren Stoff mindestens eine Verbindung der Formel



- 25 dispergiert, wobei M, x und R so sind wie im Anspruch 1 definiert.
8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Verbindung und das Polymer so sind, wie in einem der Ansprüche 2 bis 6 definiert.
9. Herstellungsgegenstand, hergestellt aus der Zusammensetzung nach einem der Ansprüche 1 bis 6.
- 30 10. Gegenstand nach Anspruch 9 in Form eines Films, dadurch gekennzeichnet, daß er eine elektrische Leitfähigkeit von mindestens etwa 10⁻⁷ Ohm⁻¹ cm⁻¹ hat.

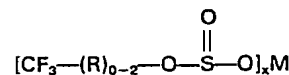
Revendications

- 35 1. Composition de poly(sulfure d'arylène), caractérisée en ce qu'elle contient au moins un composé répondant à la formule:



- 40 dans laquelle M est choisi parmi les métaux des groupes IB, IIB et VIII de la Classification Périodique, x est la valence de M et R est choisi indépendamment parmi CH₂ et CF₂, ce composé étant présent dans une quantité d'environ 3 % en poids à environ 12 % en poids par rapport au mélange de poly(sulfure d'arylène) et de composé.

2. Composition selon la revendication 1, caractérisée en ce que M est un métal du groupe IIB.
3. Composition selon la revendication 2, caractérisée en ce que M est le zinc.
4. Composition selon la revendication 3, caractérisée en ce que le composé est le trifluorométhane-sulfonate de zinc.
- 50 5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que ce composé est présent dans une quantité de 6 à 10 % en poids par rapport au poids de la composition.
6. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que ce poly(sulfure d'arylène) comprend du poly(sulfure de phénylène); en particulier dans laquelle le
- 55 poly(sulfure d'arylène) comprend au moins deux parties aromatiques réunies par des liaisons sulfure.
7. Procédé pour augmenter la conductibilité électrique d'une matière polymère, caractérisé en ce qu'on disperse dans cette matière polymère au moins un composé répondant à la formule:



- 60 dans laquelle M, x et R sont tels que définis dans la revendication 1.
8. Procédé selon la revendication 7, caractérisé en ce que ce composé et ce polymère sont tels que
- 65 définis dans l'une quelconque des revendications 2 à 6.

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9. Article manufacturé fabriqué à partir de la composition selon l'une quelconque des revendications 1 à 6.

10. Article selon la revendication 9, sous la forme d'une pellicule, caractérisé en ce qu'il a une conductibilité électrique d'au moins environ $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

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